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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
C01G 43/06, G21C 19/48, C01G 56/00

A1

(11) International Publication Number: WO 95/15921

(43) International Publication Date: 15 June 1995 (15.06.95)

(21) International Application Number: PCT/GB94/02670

(22) International Filing Date: 6 December 1994 (06.12.94)

(30) Priority Data:
9325322.7 10 December 1993 (10.12.93) GB

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(81) Designated States: JP, KR, RU, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: URANIUM HEXAFLUORIDE PURIFICATION

(57) Abstract

A method of purifying a UF_6 gas stream which comprises irradiating the UF_6 gas stream with laser radiation in a vessel in order to selectively convert fluoride impurities in the gas stream to involatile products, removing the purified UF_6 gas stream from the vessel and separately removing the impurities from the vessel.

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Uranium hexafluoride purification

This invention relates to the purification of gaseous uranium hexafluoride (UF_6) and, more particularly, to the removal of fluoride impurities from a UF_6 gas stream.

In the reprocessing of irradiated nuclear reactor fuel to produce a recycled uranium feedstock which is fluorinated to yield UF_6, a number of impurities are usually present which, upon fluorination of the feedstock, can form fluorides with volatilities similar to that of UF_6. For example, a feedstock deriving from irradiated commercial nuclear reactor fuel contains the transuranic elements Np, Pu and Am as well as the transition elements Tc, Rh and Ru. The transuranic elements typically constitute about 0.95 weight per cent on a metals basis and the aforementioned transition elements constitute about 0.38 weight per cent. Uranium is usually present at a level of about 96 weight per cent.

While the fluorides of the aforementioned transition elements generally have volatilities sufficiently different from that of UF_6 to permit separation by fractional distillation, the fluorides neptunium hexafluoride (NpF_6) and plutonium hexafluoride (PuF_6) do not, and consequently remain in the UF_6 gas stream following processing by fractional distillation.

Previously known methods for the removal of fluoride impurities from a uranium feedstock arising from irradiated nuclear reactor fuel have involved a number of techniques. In some instances the feedstock has been contacted with an aqueous solution prior to the formation of UF_6. This has the disadvantage of resulting in an increase in the volume of radioactive waste. In other instances, alkali metal fluorides have been employed to separate the impurities by selective sorption. Such a process again leads to an increase in radioactive waste products.

Other known processes include that described in US Patent number 4,364,906 in which calcium carbonate has been used as a trapping agent to purify a UF_6 gas stream. However, such a method tends to produce large volumes of waste products. US Patent Number 3,806,579 describes the distillation of impurities of MoF_6 and WF_6 from UF_6. US Patent Number 4,311,678 describes the use of a brominating agent to remove deposits of UF_6 hydrolysis products from apparatus in which UF_6 is handled. Such a process would result in the loss of some UF_6 as well as the impurities. A somewhat more successful technique is disclosed in US Patent number 4,555,318 in which a UF_6 gas stream is contacted with a bed of solid UF_5. The technique relies on the reduction of gaseous NpF_6 by UF_5 to remove the impurity, thereby creating solid NpF_5 in the process. It is indicated that this process is not an efficient one and it is likely that the required reduction and removal of the impurity is not the only process which occurs. A similar approach is described in European Patent numbers 0 087 358 and 0 088 006 in which PbF_2 and CoF_2 are employed in a manner analogous to that described for UF_5. The use of a solid fluoride bed to remove impurities will necessarily create large volumes of solid wastes which must subsequently be treated. It is also known that the use of CoF_2 is not a particularly efficient method for the removal of NpF_6. Both of these methods suffer from the disadvantages of poor efficiency and high waste production.

It is an object of the present invention to provide a method for the purification of a UF_6 gas stream without a concomitant increase in the volume of waste products.

According to a first aspect of the present invention there is provided a method of purifying a UF_6 gas stream, the method comprising irradiating the UF_6 gas stream with laser radiation in a vessel in order to selectively convert fluoride impurities in the gas stream to

involatile products, removing the purified UF_6 gas stream from the vessel and separately removing the impurities from the vessel.

The fluoride impurities in the UF_6 gas stream may comprise NpF_6 and PuF_6.

It is known that each of the molecules UF_6, NpF_6 and PuF_6 exhibits a broad intense absorption in the region above energies of about 20,000cm^{-1} as illustrated below and that the molecules dissociate at energies in the region 30,000 cm^{-1} to 20,000 cm^{-1} also as illustrated below. In addition, however, the molecules NpF_6 and PuF_6 absorb into discrete transitions at energies below about 20,000 cm^{-1}; notably around 10,000 cm^{-1} to 7,000 cm^{-1} for NpF_6 and around 13,000 cm^{-1} to 9,000 cm^{-1} for PuF_6. Therefore, there exists the possibility of selectively exciting NpF_6 and PuF_6 molecules by laser irradiation in order to effect their separation from the UF_6 gas stream.

Preferably, the UF_6 gas stream is irradiated with laser radiation in three different wavelength bands, eg from three separate laser sources, in order to selectively excite the NpF_6 and PuF_6 impurities.

Desirably, a combination of laser energies may be chosen so that the NpF_6 and PuF_6 impurities in the UF_6 gas stream each absorb two photons from the radiation field so that NpF_6 and PuF_6 molecules are excited above their dissociation thresholds and thereby dissociate into involatile lower fluorides and fluorine atoms. The UF_6 molecules are not dissociated by the radiation field.

The UF_6 gas stream is preferably irradiated with laser radiation in two stages : in a first stage the NpF_6 and PuF_6 molecules are excited by a laser radiation field having energies in the range 10,000 cm^{-1} to 7,000 cm^{-1} and 13,000 cm^{-1} to 9,000 cm^{-1} respectively and, more preferably, by laser radiation having energies of 9528 cm^{-1} and 9583 cm^{-1} respectively; in a second stage the NpF_6 and PuF_6 molecules are excited with laser

radiation having an energy in the range 17,500 cm^{-1} to 24,000 cm^{-1} and more preferably, laser radiation having an energy of 19,570 cm^{-1}, the two stage irradiation thereby exciting the NpF_6 and PuF_6 molecules above their dissociation thresholds so as to dissociate the said molecules into involatile products comprising lower fluorides which deposit in the vessel as solids.

The energy of the laser radiation in the second stage may be advantageously of an energy such that the radiation is not absorbed by UF_6 molecules and the UF_6 gas thereby remains unaffected.

Conveniently, in the first laser irradiation stage, the NpF_6 and PuF_6 molecules may be respectively irradiated by two (separate) solid state lasers and, preferably, the lasers may be Nd^{3+}-doped solid state lasers. More preferably, the NpF_6 molecules may be irradiated by a Nd^{3+}-doped fluorozirconate laser or a Nd^{3+}-doped aluminium fluoride glass laser, whereas the PuF_6 molecules may be irradiated by a Nd^{3+}-doped fluoroberyllate glass laser.

In the second laser irradiation stage, the NpF_6 and PuF_6 molecules may be conveniently irradiated by radiation from a copper vapour laser or a high power argon-ion laser.

Advantageously, removal of the involatile products from the vessel may be effected by contacting the said products with one or more suitable fluorinating agents to form gaseous products. Chemical fluorinating agents may be used and suitable chemical fluorinating agents may include IF_7, BrF_3 and ClF_3. As an alternative, photochemical fluorinating agents may be used in conjunction with irradiation from a source of ultra violet energy to form gaseous products. Suitable photochemical fluorinating agents may include F_2 and ClF.

According to another aspect of the present invention there is provided a system for the purification of a UF_6 gas stream by the method of the first aspect, the system

comprising a reaction vessel, a source of unpurified gaseous UF_6, a source of a gaseous fluorinating agent, for example, fluorine, means for admitting said unpurified UF_6 and said fluorinating agent into the reaction vessel, means for irradiating the contents of the reaction vessel, means for allowing gases to exit the reaction vessel, means for separating the gases exiting the reaction vessel, and means for collecting the separated gases.

Preferably, the contents of the reaction vessel may be irradiated by a combination of laser and ultra violet sources.

Conveniently, the reaction vessel may have a window which is optically transparent to the energies of the laser and ultra violet radiation from the sources.

Advantageously, a number of the said systems may be cascaded in series in order to produce high purity UF_6.

A further advantage would be that sections of a cascaded system could be switched out of the process during maintenance and to allow the removal of accumulated impurities.

The method of the present invention is particularly beneficial in the purification of a UF_6 gas stream avoiding the need for wet chemical processing and without the generation of large volumes of waste products which require subsequent treatment and/or storage.

It has been recognised in US Patent number 4,670,239 that it is possible to photodissociate PuF_6 directly to PuF_5 using visible radiation. However, the photodissociation has not been used to separate PuF_6 gas from other species but simply as a method for the preparation of PuF_5.

Embodiments of the present invention will now be described, by way of example only, with reference to the accompanying drawings, in which:

Figure 1 is a graph of energy versus absorption cross section showing absorption spectra of the molecules UF_6, NpF_6 and PuF_6;

Figure 2 shows a schematic representation of the absorption of the molecules UF_6, NpF_6 and PuF_6;

Figure 3 shows a schematic representation of a system for the purification of a UF_6 gas stream, and

Figure 4 shows, to an enlarged scale, a part sectional view of part of the system of Figure 3.

Referring now to Figure 1, the absorption spectra of the molecules UF_6, NpF_6 and PuF_6 are shown in the region 50000 cm^{-1} to 5000 cm^{-1}. Figure 2 shows the absorption of each of the aforementioned molecules represented schematically along with their measured dissociation energies. As can be seen, each of the molecules exhibits a broad, intense absorption in the region above about 20,000 cm^{-1}, and the molecules dissociate at energies in the region 30,000 cm^{-1} to 20,000 cm^{-1}. In addition, as shown in Figure 2, the molecules NpF_6 and PuF_6 absorb into discrete transitions at energies below 20,000 cm^{-1} (notably 10,000 cm^{-1} to 7,000 cm^{-1} for NpF_6 and 13,000 cm^{-1} to 9,000 cm^{-1} for PuF_6).

Referring now to Figure 3, a system 10 is shown for the purification of a UF_6 gas stream making use of the absorption characteristics of NpF_6 and PuF_6. In the system 10, a reaction vessel 12 is supplied with unpurified UF_6 gas from a source 14 and fluorine gas from a source 16. The UF_6 source 14 is connected by a line 18 to a valve 20 having a line 22 to an inlet line 24 which is connected to the reaction vessel 12. The fluorine source 16 is connected by a line 26 to a valve 28 having a line 30 to the inlet line 24.

An outlet line 32 connects the reaction vessel 12 to a valve 34. A line 36 extends from the valve 34 and passes through a cold trap 38 to connect with a four-way valve 40. The valve 40 connects with a further three lines 42,

44 and 46 which respectively connect the valve 40 to three reservoirs 48, 50 and 52.

Located in close proximity to one end of the reaction vessel 12 are three laser radiation sources 54, 56 and 58, and a source of ultra violet radiation 60.

As shown in Figure 4 the reaction vessel 12 is connected to the inlet line 24 near to one of its ends and to the outlet line 32 near to its other end. The reaction vessel 12 is made of a material such as nickel or monel which is resistant to UF_6. One end of the reaction vessel 12 has a window 62 made from a material which is optically transparent to the energies of the laser and ultra violet radiation from the sources 54, 56, 58, 60. A suitable material for the window 62 is magnesium fluoride. The reaction vessel 12 serves as a photolysis cell in which radiation from the sources 54, 56, 58, 60 passes through the window 62 to contact with material in the reaction vessel 12. At the connections to the inlet line 24 and to the outlet line 32, the reaction vessel 12 is provided with filters 64 which serve to protect the external gas circuit from any particulate matter produced in the reaction vessel 12.

In operation of the system 10 of Figure 3, valves 20 and 28 are initially closed, valve 34 is in an open position and valve 40 is operated so as to connect lines 36 and 42. Unpurified UF_6 is admitted to the reaction vessel 12 by opening valve 20 so that a UF_6 gas stream flows from the UF_6 source 14 through lines 18, 22 and 24 into the vessel 12. In the reaction vessel 12, unpurified UF_6 is subjected to irradiation from the laser sources 54, 56 and 58, the laser radiation passing into the vessel 12 through the window 62 (see Figure 4). A combination of laser energies is chosen so that the NpF_6 and PuF_6 impurities in the UF_6 gas stream each absorb two photons from the radiation field. In this way the NpF_6 and PuF_6 molecules are excited above their dissociation thresholds

and thereby dissociate into involatile lower fluorides and fluorine atoms. The UF_6 molecules are unaffected by the radiation field.

The laser irradiation is carried out in two stages. In the first stage NpF_6 molecules are excited by laser radiation having an energy of 9528 cm^{-1} from a Nd^{3+}-doped fluorozirconate laser 54 (or a Nd^{3+}-doped aluminium fluoride glass laser), and PuF_6 molecules are excited by laser radiation having an energy of 9583 cm^{-1} from a Nd^{3+}-doped fluoroberyllate glass laser 56. In the second stage the NpF_6 and PuF_6 molecules are excited with laser radiation having an energy of 19,570 cm^{-1} from a copper vapour laser 58. The laser irradiation causes decomposition of the NpF_6 and PuF_6 into lower valency fluorides, which are deposited in the vessel 12 as involatile solids, and fluorine gas.

The UF_6 gas stream which is now free from Np and Pu impurities, but which contains fluorine gas from the photochemical reaction, is fed via lines 32 and 34 through the cold trap 38 in which the UF_6 condenses. The fluorine, which does not condense in the cold trap 38, passes through lines 36 and 42 into the reservoir 48 where it is collected. To remove the purified UF_6 from the cold trap 38, valve 34 is closed and valve 40 is operated so as to connect lines 36 and 44. The cold trap 38 is warmed to a temperature at which UF_6 volatilises (approximately 57°C) and the purified UF_6 is collected in the reservoir 50.

Periodically, valve 20 is closed to interrupt the flow of unpurified UF_6 gas from the source 14 to the reaction vessel 12. Purified UF_6 and fluorine are removed from the reaction vessel 12 to the reservoirs 48 and 50 respectively in the manner described hereinbefore. Valve 28 is opened and fluorine gas is fed into the reaction vessel 12 from the fluorine source 16 via lines 26, 30 and 24. The reaction vessel 12 and its contents are

irradiated by the ultra violet source 60, the ultra violet radiation passing into the vessel 12 through the window 62. The involatile solid impurities in the vessel 12 are thereby photochemically fluorinated to NpF_6 and PuF_6. Valve 40 is operated so as to connect lines 36 and 42 and valve 34 is now opened. The gases leaving the reaction vessel 12 are fed via lines 32 and 36, through the cold trap 38 where the NpF_6 and PuF_6 condense. Any unreacted fluorine does not condense in the cold trap 38 and passes through lines 36 and 42 into the reservoir 48 where it is collected. To remove the NpF_6 and PuF_6 from the cold trap 38, valve 34 is closed and valve 40 is operated so as to connect lines 36 and 46. The cold trap 38 is warmed to a temperature at which the NpF_6 and PuF_6 volatilise (approximately 60°C) and they are then collected in the reservoir 52.

In order to achieve the economical removal of impurities from a UF_6 gas stream to produce purified UF_6 of an acceptable quality for use in gaseous diffusion plants, it may be necessary to cascade several of the hereinbefore described systems in series. Cascading would have the additional advantage of enabling sections of the overall system to be switched out of the process during maintenance and during the periodic removal of accumulated impurities.

In an alternative method of purifying a UF_6 gas stream NpF_6 and PuF_6 may be dissociated independently and are collected in separate reservoirs. Although PuF_6 can be photodissociated in a two-photon process as described above, the dissociation can be carried out more simply using a single photon process.

In the alternative method PuF_6 molecules in the gas stream are photodissociated in a reactor using laser radiation of a relatively low energy such that the irradiation has no effect on the UF_6 and NpF_6 molecules. The involatile solid fluoride product can then be

collected and treated as required. The UF_6 gas stream containing the NpF_6 impurity passes into a second reactor in which the NpF_6 is excited and photodissociated using the two-photon process as described above. The second involatile solid photoproduct is collected and treated as required and the purified UF_6 gas stream passes to a reservoir for collection.

Claims

1. A method of purifying a UF_6 gas stream, the method comprising irradiating the UF_6 gas stream with laser radiation in a vessel in order to selectively convert fluoride impurities in the gas stream to involatile products, removing the purified UF_6 gas stream from the vessel and separately removing the impurities from the vessel.

2. A method as in Claim 1 and wherein the fluoride impurities in the UF_6 gas stream comprise NpF_6 or PuF_6 or both.

3. A method as in Claim 1 or Claim 2 and wherein the UF_6 gas stream is irradiated with laser radiation in three different wavelength bands, from three separate laser sources, in order to excite selectively NpF_6 and PuF_6 impurities.

4. A method as in any one of the preceding Claims and wherein a combination of laser energies is employed so that the NpF_6 and PuF_6 impurities in the UF_6 gas stream each absorb two photons from the radiation field so that NpF_6 and PuF_6 molecules are excited above their dissociation thresholds and thereby dissociate into involatile lower fluorides and fluorine atoms.

5. A method as in any one of the preceding Claims and wherein the UF_6 molecules are not dissociated by the radiation field.

6. A method as in any one of the preceding Claims and wherein the UF_6 gas stream is irradiated with laser radiation in two stages thereby exciting the NpF_6 and PuF_6 molecules above their dissociation thresholds so as to dissociate the said molecules into involatile products comprising lower fluorides which deposit in the vessels as solids.

7. A method as in Claim 6 and wherein, in a first stage, the NpF_6 and PuF_6 molecules are excited by a laser

radiation field having energies in the range 10000 cm^{-1} to 7000 cm^{-1} and 13000 cm^{-1} to 9000 cm^{-1} respectively.

8. A method as in Claim 7 and wherein the NpF_6 and PuF_6 molecules are excited by laser radiation having energies of 9528 cm^{-1} and 9583 cm^{-1} respectively.

9. A method as in Claim 7 or Claim 8 and wherein the NpF_6 and PuF_6 molecules are respectively irradiated by two separate solid state lasers.

10. A method as in Claim 9 and wherein the lasers are Nd^{3+}-doped solid state lasers.

11. A method as in Claim 10 and wherein the NpF_6 molecules are irradiated by a Nd^{3+}-doped fluorozirconate laser or a Nd^{3+}-doped aluminium fluoride glass laser, and the PuF_6 molecules are irradiated by a Nd^{3+}-doped fluoroberyllate glass laser.

12. A method as in Claim 6 and wherein, in a second stage, the NpF_6 and PuF_6 molecules are excited with laser radiation having an energy in the range 17500 cm^{-1} to 24000 cm^{-1}.

13. A method as in Claim 12 and wherein the NpF_6 and PuF_6 molecules are excited with laser radiation having an energy of 19570 cm^{-1}.

14. A method as in Claim 12 or Claim 13 and wherein the laser radiation is of an energy such that the radiation is not absorbed by UF_6 molecules and the UF_6 gas thereby remains unaffected.

15. A method as in any one of Claims 12 to 14 and wherein the NpF_6 and PuF_6 molecules are irradiated by radiation from a copper vapour laser or a high power argon-ion laser.

16. A method as in Claim 1 and wherein removal of the involatile products from the vessel is effected by contacting the said products with one or more suitable fluorinating agents to form gaseous products.

17. A method as in Claim 16 and wherein the fluorinating agents are chemical fluorinating agents.

18. A method as in Claim 17 and wherein the chemical fluorinating agents include IF_7, BrF_3 and ClF_3.

19. A method as in Claim 16 and wherein photochemical fluorinating agents are used in conjunction with irradiation from a source of ultra violet energy to form gaseous products.

20. A method as in Claim 19 and wherein the photochemical fluorinating agents include F_2 and ClF.

21. A system for the purification of a UF_6 gas stream by the method described in any one of Claims 1 to 20, the system comprising a reaction vessel, a source of unpurified gaseous UF_6 , a source of a gaseous fluorinating agent such as fluorine, means for admitting said unpurified UF_6 and said fluorinating agent into the reaction vessel, means for irradiating the contents of the reaction vessel, means for allowing gases to exit the reaction vessel, means for separating the gases exiting the reaction vessel, and means for collecting the separated gases.

22. A system as in Claim 21 and wherein the contents of the reaction vessel are irradiated by a combination of laser and ultra violet sources.

23. A system as in Claim 21 or Claim 22 and wherein the reaction vessel has a window which is optically transparent to the energies of the laser and ultra violet radiation from the sources.

24. A system as in any one of Claims 21 to 23 and wherein a number of the said systems are cascaded in series in order to produce high purity UF_6.

25. A method of purifying a UF_6 gas stream substantially as hereinbefore described with reference to Figure 3 and Figure 4 of the accompanying drawings.

26. A system for the purification of a UF_6 gas stream substantially as hereinbefore described with reference to Figure 3 and Figure 4 of the accompanying drawings.

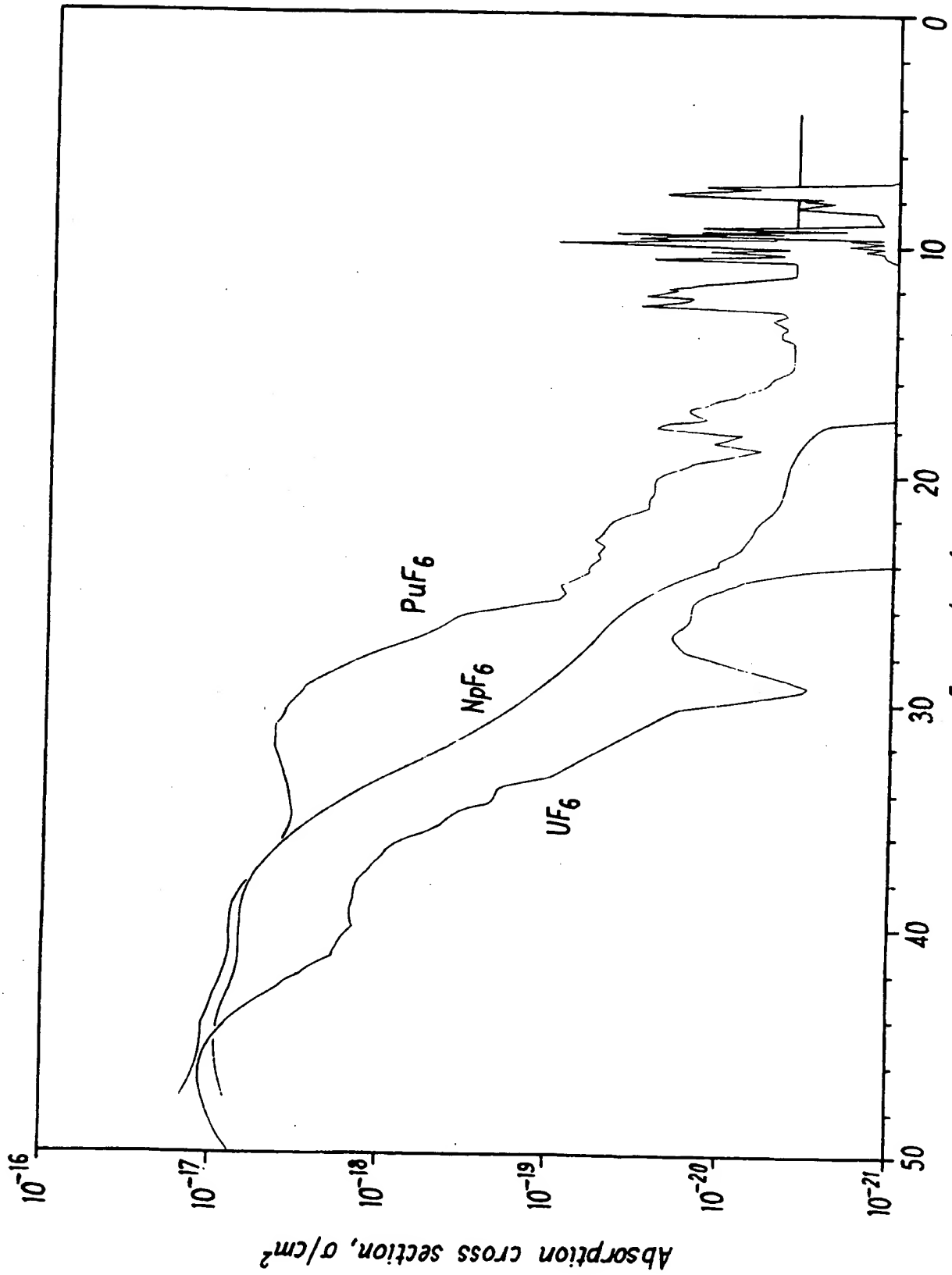

Fig. 1

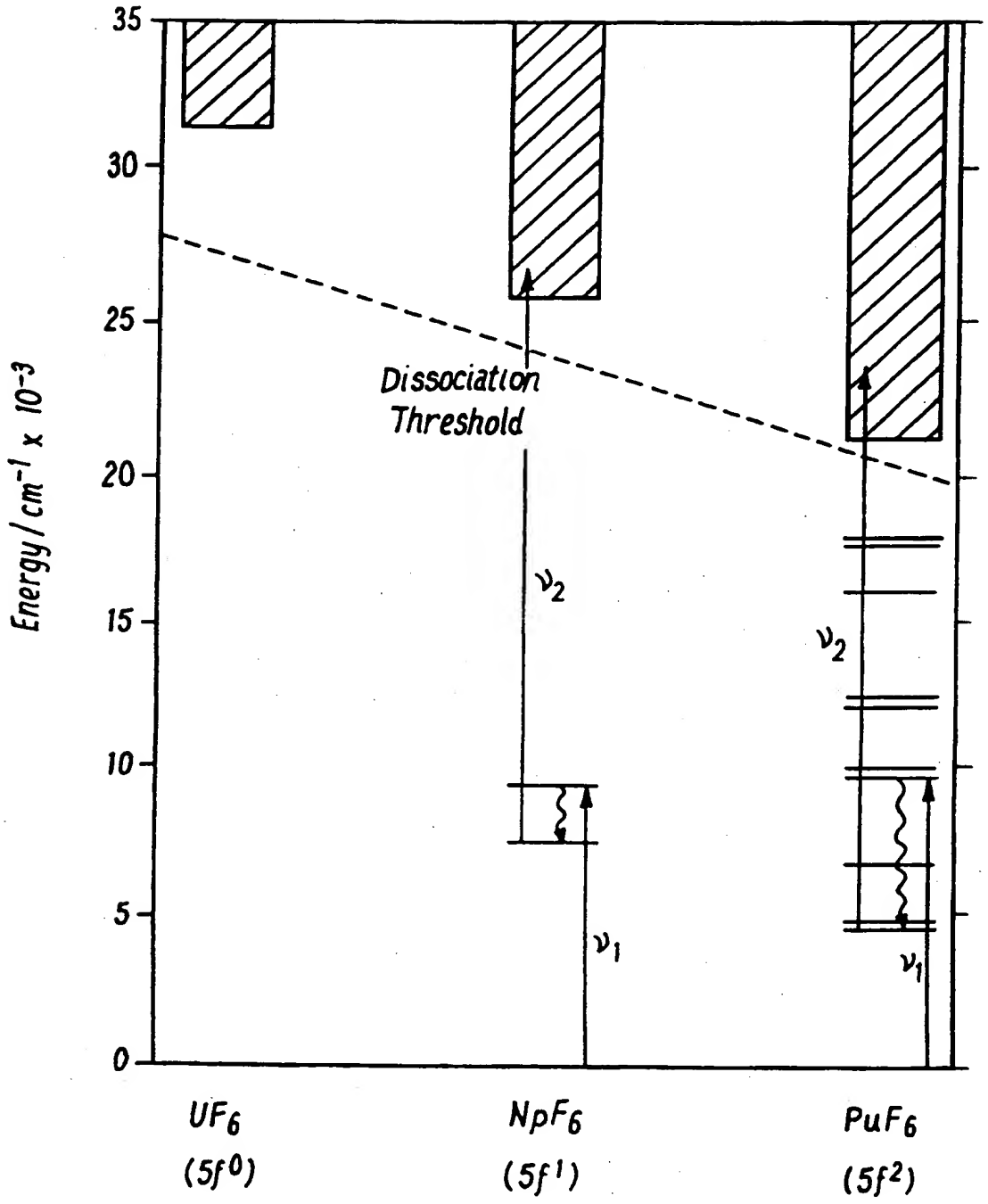

FIG. 2

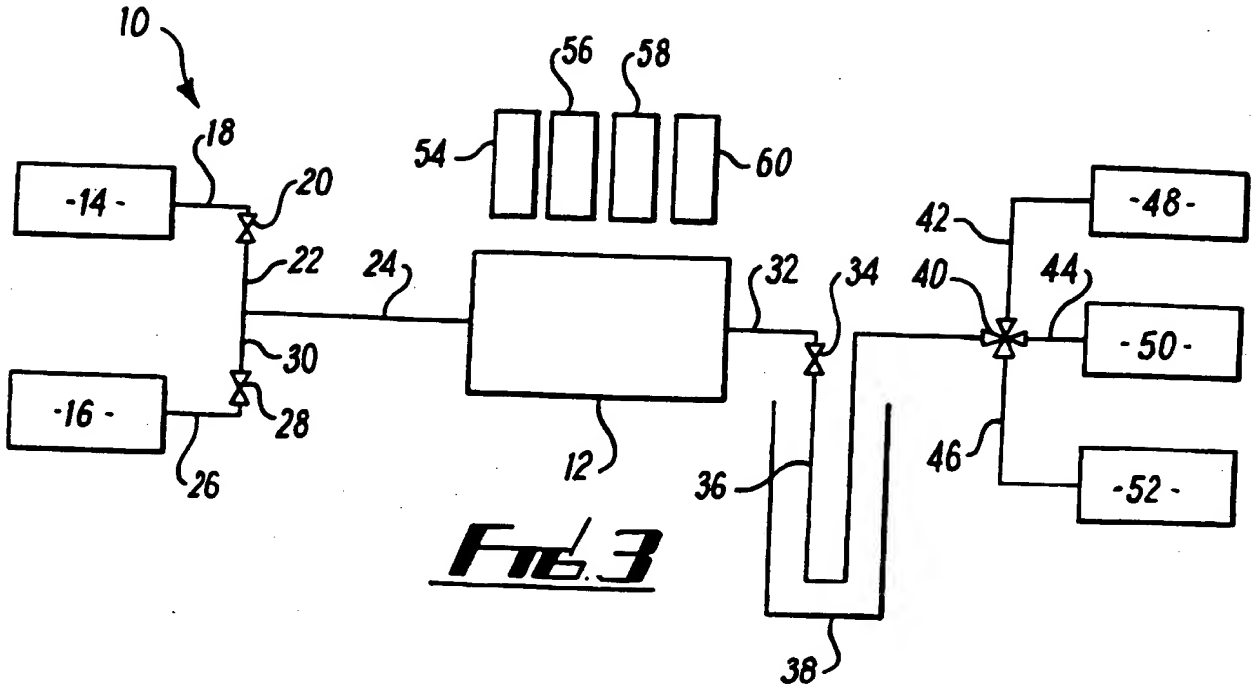

FIG. 3

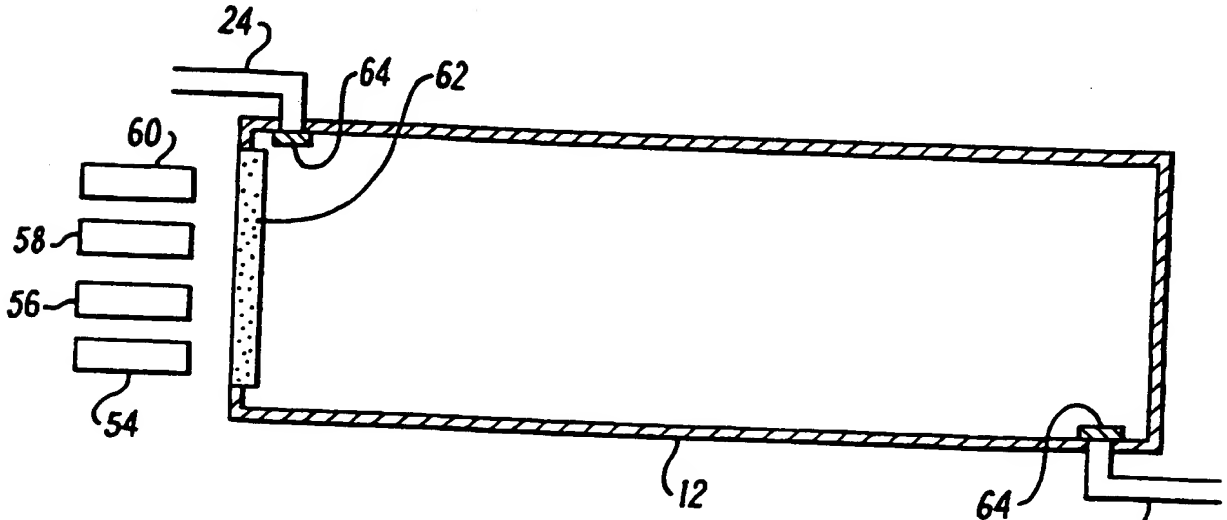

FIG. 4